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Seasonal variation in tissue-borne heavy Metal(loid)s in herbaceous plants growing in contaminated soils developed from industrial wastes of industrial revolution age

Obinna Elijah Nworie [a], Chuxia Lin [a,b,*]

[a] School of Science, Engineering and Environment, University of Salford, Greater Manchester M5 4WT United Kingdom
[b] Faculty of science, Engineering and Built Environment, Deakin University, Burwood, Melbourne, Victoria, Australia

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ABSTRACT

A 1-year monitoring program was performed to examine the seasonal variation in shoot-borne heavy metal(loid)s in a dominant herbaceous plant species (creeping bentgrass) growing in contaminated soils developed from industrial wastes of Industrial Revolution age in Greater Manchester, UK. Heavy metal(loid)s in soil and plant tissues were quantified by inductively coupled plasma optical emission spectrometry (ICP-OES) after microwave-assisted acid digestion. The results show that different heavy metal(loid)s in the shoot tissue had different seasonal variation patterns. Seasonal shoot cutting-regrowth did not markedly affect the accumulation of various heavy metal(loid)s in the shoots. The concentration of shoot-borne heavy metal(loid)s was below the maximum tolerable level set for cattle except for Cd during spring-summer. The seasonal variation pattern for removal rate of Cd, Cr, Cu, Pb and Zn was strongly controlled by seasonal variation in biomass yield. The heavy metal(loid) removal from the soils via seasonal shoot harvest was 0.11, 0.56, 0.57, 3.56, 60.4, 0.34, 0.27 and 12.3 mg/m^2 for As, Cd, Cr, Cu, Mn, Ni, Pb and Zn, respectively. It is estimated that during the 1-year monitoring period, only 0.0002, 0.4014, 0.0142, 0.0423, 0.1627, 0.0154, 0.0008 and 0.1840% of the total metal(loid)s were removed from the soil by the plant shoots for As, Cd, Cr, Cu, Mn, Ni, Pb and Zn, respectively. Phytoextraction literally had negligible effects on removing the investigated heavy metal(loid)s from the contaminated soils except for Cd, Mn and Zn. The average bioaccumulation factor for the investigated heavy metal(loid)s was in the following decreasing order: Zn > Mn > Cu > Cr > Ni > Cd > Pb > As. The translocation factor for Cd was over 10 under either non-regrowth or cutting-regrowth conditions although the bioaccumulation factor was smaller than 0.5. The research findings obtained from this study have implications for risk assessment and management of the industrial waste-turned contaminated soils.

1. Introduction

The presence of scattering contaminated sites is an important characteristic of industrial cities, particularly the historical industrial centres where dumping of industrial wastes was hardly regulated (BenDor et al., 2011; Njue et al., 2012; Martuzzi et al., 2014). Since these environmental footprints are often in close proximity to residential areas, their impacts on urban ecosystem and human health are potentially remarkable. Understanding the environmental risk that these contaminated lands pose to the residents living in the surrounding areas is crucial for developing sound management strategies to minimize the adverse environmental impacts. We have investigated a contaminated site in the Greater Manchester (UK), the key player of the first Industrial Revolution. It was found that the soils in the investigated areas had high levels of arsenic and heavy metals, which could be exported to the surrounding atmospheric and aquatic environments through dust formation and during flooding (Mukwaturi and Lin, 2015; Qin et al., 2016; Nworie et al., 2019).

Plant uptake of heavy metal(loid)s from contaminated soils is an essential part of environmental risk assessment for contaminated lands (Qin et al., 2021). Accumulation of potentially toxic heavy metal(loid)s in the aerial portion of the plants could cause dispersion of these elements into other environmental compartments when wild animals consume the forage or when the leaf litters are transported out of the

* Corresponding author at: Faculty of Science, Engineering and Built Environment, Deakin University, Burwood, Melbourne, VIC, Melbourne, Australia.
E-mail address: chu.lin@deakin.edu.au (C. Lin).

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contaminated site by action of wind and water. Knowledge of plant tissue-borne heavy metal(loid)s is also needed for evaluating the potential of the herbaceous plants to be used for grazing purpose or phytoremediation to clean up the contaminated soils (Green et al., 2014).

Translocation of heavy metal(loid)s from soils to plant aerial portion *via* roots is determined by many factors. The concentration of heavy metal(loid)s in the soils plays an important role in supplying heavy metal(loid)s for the plant roots (Muchuweti et al., 2006). However, the rate of heavy metal(loid) uptake is not determined by the total amount of heavy metal(loid)s present in the soils since the majority of soil-borne heavy metal(loid)s may not be in phytoavailable forms (Cataldo and Wildung, 1978). This is particularly true for non-acidic soils where heavy metal(loid)s are in practically insoluble forms (Markiewicz-Patkowska et al., 2005; Mukwaturi and Lin, 2015). In such situations, mobilization of soil-borne heavy metal(loid)s is mainly driven by low-molecular-weight organic acids (LMWOAs) released from plant roots (Onireti and Lin, 2016). Work using the soils collected from the study site showed that significant amounts of heavy metal(loid)s were mobilized from the soils by typical low-molecular-weight organic acids such as citric, oxalic and malic acids (Onireti and Lin, 2016). Our previous investigation involving 27 herbaceous plant species at the study sites indicated that both bioaccumulation factor and translocation factor were highly variable among the investigated plants (Nworie et al., 2019). This is attributable to the difference in soil characteristics and capacity of individual plants to take the heavy metal(loid)s from the soils. It is well recognized that different plants tend to release different types of dominant low-molecular-weight organic acids in their exudates and the chemical composition of root exudates of a specific plant may change from growth stage to growth stage (Jones, 1998; Haoliang et al., 2007; Mucha et al., 2010). This could have impacts on the uptake of soil-borne heavy metal(loid)s by the plants, leading to seasonal variation in plant tissue-borne heavy metal(loid)s.

There have been interests to understand the seasonal variation in plant tissue-borne trace elements. Kim and Fergusson (1994) reported on seasonal variations in the concentrations of cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) in leaves of the horse chestnut (*Aesculus hippocastanum* L.). Lodenius (2002) investigated seasonal variation in the leaf-borne cadmium of vascular plants growing in non-contaminated soils. Brekken and Steinnes (2004) observed the change in concentrations of cadmium and zinc in native pasture plants from early June to early September. Kim and Kim (2018) showed the seasonal variations of metal (Cd, Pb, Mn, Cu, Zn) accumulation in Salix subfragilis growing in unpolluted wetlands. Lin et al. (2020) observed changes in the leaf and branch trace elements of *Pinus massoniana* Lamb in response to drought during a 3-year period. Other available reports on seasonal variation in plant tissue-borne heavy metal(loid)s included seaweeds (Villares et al., 2002) and aquatic plants (Duman and Obali, 2008). Reports on trace elements in grasses have been focussed on forage quality for grazing animals or wild animals. However, these investigations were largely conducted in non-contaminated soils. (Khan et al., 2006; Nedjimi, 2020) or soils contaminated by a limited number of heavy metals with a monitoring period less than 1 year (Deram et al., 2006). So far, it seems that there has been no detailed investigation done on seasonal variation of heavy metal(loid)s in herbaceous plants growing in multi-contaminated soils.

Phytoextraction is one of remediation strategies for clean-up of heavy metal(loid)-contaminated soils (Wood et al, 2016). However, most heavy metal(loid)-hyperaccumulators have a low biomass-producing capacity (Liang et al., 2009). Therefore, the costs associated with long-term maintenance of the farming practices for growing the hyperaccumulating plants and the loss of land value for agricultural production during the period of remediation, let alone the additional costs required for the treatment of the potentially hazardous harvested biomass could make it less cost-effective (Niu and Lin, 2021). Therefore, instead of growing hyperaccumulating plants, the use of naturally occurring plant species with high biomass-yielding capacity to extract soil-borne heavy metal(loid)s may be a sensible alternative for soil clean-up because it could achieve the removal of heavy metal(loid)s from the contaminated soils at a level comparable to low biomass-yielding hyperaccumulating plants but at no cost required for the treatment of the potentially hazardous harvested plant biomass. The harvested biomass may be used beneficially e.g., as fuel, feedstock for biochar production or animal feed if the levels of trace elements are below the permissible limits. To evaluate the feasibility of this approach, an understanding of temporal variation in heavy metal(loid)s in the seasonally harvested plant biomass is required. This knowledge is currently lacking.

The objectives of this study were therefore to (a) monitor seasonal variation in shoot-borne heavy metal(loid)s of herbaceous plants growing in contaminated soils with and without seasonal shoot cutting-regrowth arrangement, (b) evaluate the effect of harvest frequency on the removal effect of soil-borne heavy metal(loid)s, and (c) evaluate the environmental risk of heavy metal(loid)-containing plant shoots.

2. Materials and methods

2.1. Description of the monitoring site

The site selected for the monitoring program is located in Failsworth, part of the Greater Manchester (latitude: 53.515889°N; longitude: 002.155625°W) in the Northwest England (Fig. 1). During the first Industrial Revolution, the area was predominantly associated with bleaching and dyeing works as an important finishing process of manufacturing cotton fabrics. Other industrial activities included print and brick works. Several landfill sites were in use for disposal of various wastes generated from the industrial production. These historically industrial activities with unregulated waste disposal practices created a legacy of heavy metal(loid) contamination in the area, which represents a potential risk to human health and ecological system (Groundwork Oldham and Rochdale, 2008).

Previous investigation identified a sub-area (locally known as "White Hills") with the soils consisting of pale-yellow materials derived from the dumped solid wastes (Fig. 1). The soils contained elevated levels of arsenic, lead and other heavy metals. And the herbaceous plants growing in the soils tended to take up heavy metal(loid)s from the contaminated soils and accumulate in the shoots (Nworie et al., 2019). It was considered that the sub-area be an ideal site for carrying out a monitoring program to observe the seasonal variation in plant tissue-borne heavy metal(loid)s. Within the investigated area, creeping bentgrass (*Agrostis stolonifera*) dominated the herbaceous plants.

2.2. Design of the monitoring program

To account for horizontal variation in soil characteristics within the investigated area, five monitoring locations (marked as LW1, LW2, LW3, LW4 and LW5 in Fig. 1) were established. At each monitoring location, a 6 m x 6 m plot with dominant presence of creeping bentgrass was selected for monitoring the characteristics of the plants. Within each monitoring plot, 4 subplots (1 m x 1 m) were used to harvest the shoot portion at different seasons during the period from August 2018 to May 2019. The shoots of all plants in Subplots 1, 2, 3 and 4 were harvested in August 2018, November 2018, February 2019 and May 2019, respectively. Subplot 1 was also used to collect the shoot portion at the end of the 3 cutting-regrowth cycles (*i.e.* August to November 2018, November 2018 to February 2019, and February 2019 to May 2019). To avoid disturbance of the monitored plots, soil (0-15 cm) and root samples were only collected at the end of the monitoring period (*i.e.* May 2019).

2.3. Laboratory methods

In the laboratory, the fresh biomass of each subplot was determined by weighing in a weighing balance after being washed with tap water

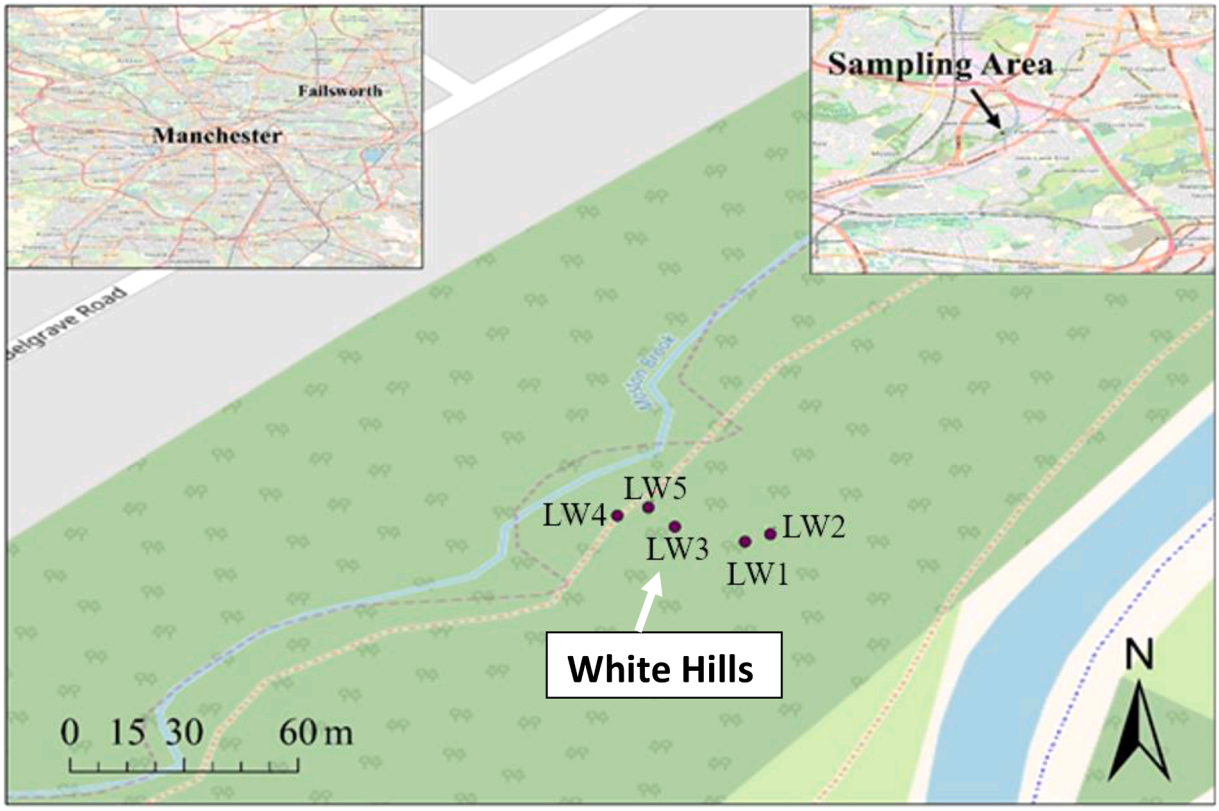

Fig. 1. Map showing the five monitoring locations covering the major part of "White Hills" at the Moston Brook Closed Landfill site of the Greater Manchester, Northwest England

followed by distilled water, wiped with a paper towel, and air-dried. A portion (150 g) of the air-dried plant sample from each subplot was oven-dried at 65 C until a constant weight was achieved. After oven-drying, the dry weight of the shoot sample was determined. Each of the oven-dried plant tissues was ground using an electrical plant tissue pulverizer and stored in a sealable bag prior to analysis.

The root samples collected at the end of the monitoring program were washed by tap water followed by distilled water, and then dried with a paper towel prior to oven-drying at 65 ℃ until a constant weight was achieved. All the oven-dried root samples collected from each subplot at each location were mixed to form a composite sample to represent that location. The root sample was ground using an electrical plant tissue pulverizer and stored in a sealable plastic bag prior to analysis. The soil samples collected at the end of the monitoring program were oven-dried at 40 ℃ for 5 days, ground to pass 2 mm sieve and then stored in sealable plastic bags prior to analysis.

For determination of heavy metal(loid)s in the plant tissues, 0.5 g of the powdered sample was weighed and added into a microwave digestion tube, followed by adding 1 mL of 30% (m/m) H_2O_2 and 7 mL of concentrated HNO_3 solution. The tubes were fitted with bungers and closed appropriately with lids and placed into microwave carousel. The microwave digestion was done according to the procedure described in Bressy et al. (2013). After cooling, the samples were filtered using Whatman filter papers (No. 42). The filtrates were then diluted to a final volume of 50 mL with deionized water. The diluted extracts were stored at 4°C in a refrigerator prior to analysis. The concentration of heavy metal(loid)s in the extracts was determined by inductively coupled plasma optical emission spectrometry (Varian720-ES ICP-OES, Palo Alto, CA, USA).

Soil pH and electrical conductivity (EC) were measured from soil-water suspensions (1:5) using a calibrated pH meter (HANNA instruments Woonsocket RI USA) and EC meter (METTLER TOLEDO SevenCompact Conductivity meter S230), respectively. Organic matter content was determined by the loss-on-ignition method (Smith, 2013). The concentration of soil-borne heavy metal(loid)s was determined by ICP-OES after digesting 0.5 g of oven-dried soil samples with 10 mL of concentrated HNO_3 in the microwave digester. The digestion of soil samples lasted for about one hour at a maximum temperature of 180 ℃. After digestion, the digested samples were allowed to cool and filtered using Whatman filter papers (No. 42). The filtrates were then diluted to a final volume of 50 mL with deionized water. The diluted samples were stored at 4°C in a refrigerator prior to analysis. The concentrations of various heavy metal(loid)s were measured by ICP-OES (Varian720-ES).

3. Results and discussion

3.1. Characteristics of the soils at the monitored locations

The major characteristics of the soils at the five monitoring locations are given in Table 1. The mean soil pH of the five monitoring locations was 5.41 with a range of 4.92-6.13. The soils had the EC value ranging from 0.036 to 0.103 dS/m with an average of 0.060 dS/m. The organic matter content averaged at 2.63% with a range of 2.08-3.37%. All the soils had elevated concentration of arsenic with the mean value being 209 mg/kg, which is over 40 times greater than the threshold value used for evaluating contaminated agricultural soils in Europe (Tóth et al., 2016). However, the soil-borne As was highly variable with a range of 42.9-355 mg/kg. Lead was another heavy metal that had the concentration exceeding the threshold value except at Location 1. Soil-borne Cd was slightly greater than the threshold value at Locations 1 and 2 but well below the threshold value at the other locations. All other heavy metals in the soils had much lower concentration, as compared to their respective threshold values (Tóth et al., 2016).

It is interesting to note that the soil pH was closely related to EC, As and Pb (Fig. 2). As mentioned in the research method section, the soils were formed mainly from previous industrial wastes derived from

Table 1
pH, EC, organic matter content (OMC) and concentrations of various heavy metal(loid)s in the soils at the five monitoring locations (TV denotes threshold value)

Parameter	LW1	LW2	LW3	LW4	LW5	Mean ± SD	TV
pH	6.13±0.01	4.92±0.09	5.46±0.01	5.03±0.01	5.53±0.01	5.41 ± 0.48	
EC (dS/m)	0.103±0.002	0.036±0.000	0.065±0.001	0.051±0.000	0.057±0.001	0.060 ± 0.030	
OMC (%)	2.52±0.13	2.08±0.05	2.49±0.05	3.37± 0.13	2.71±0.05	2.63 ± 0.47	
As (mg/kg)	42.9±4.11	355±6.95	242±11.2	212±5.41	194±20.4	209±112	5
Cd (mg/kg)	1.18±0.67	1.12±0.48	0.33±0.16	0.36±0.06	0.11±0.00	0.62±0.49	1
Cr (mg/kg)	19.0±6.08	21.2±1.01	13.6±3.15	15.5±0.45	19.7±1.10	17.8±3.14	100
Cu (mg/kg)	21.3±1.36	34.8±1.28	18.7±0.73	85.2±2.19	27.1±0.98	37.4±27.4	100
Mn (mg/kg)	187±12.8	106±6.61	90.2±4.68	200±5.75	243 ±7.38	165±64.9	
Ni (mg/kg)	8.37±0.51	8.34±0.42	7.24±1.83	10.9±0.40	14.2±0.29	9.81±2.80	50
Pb (mg/kg)	45.7±5.92	241±27.3	151±6.39	178±8.92	128±3.75	149±71.5	60
Zn (mg/kg)	23.2±1.4	28.7±1.25	24.6±3.05	42.6±5.25	29.3±1.84	29.7±7.68	200

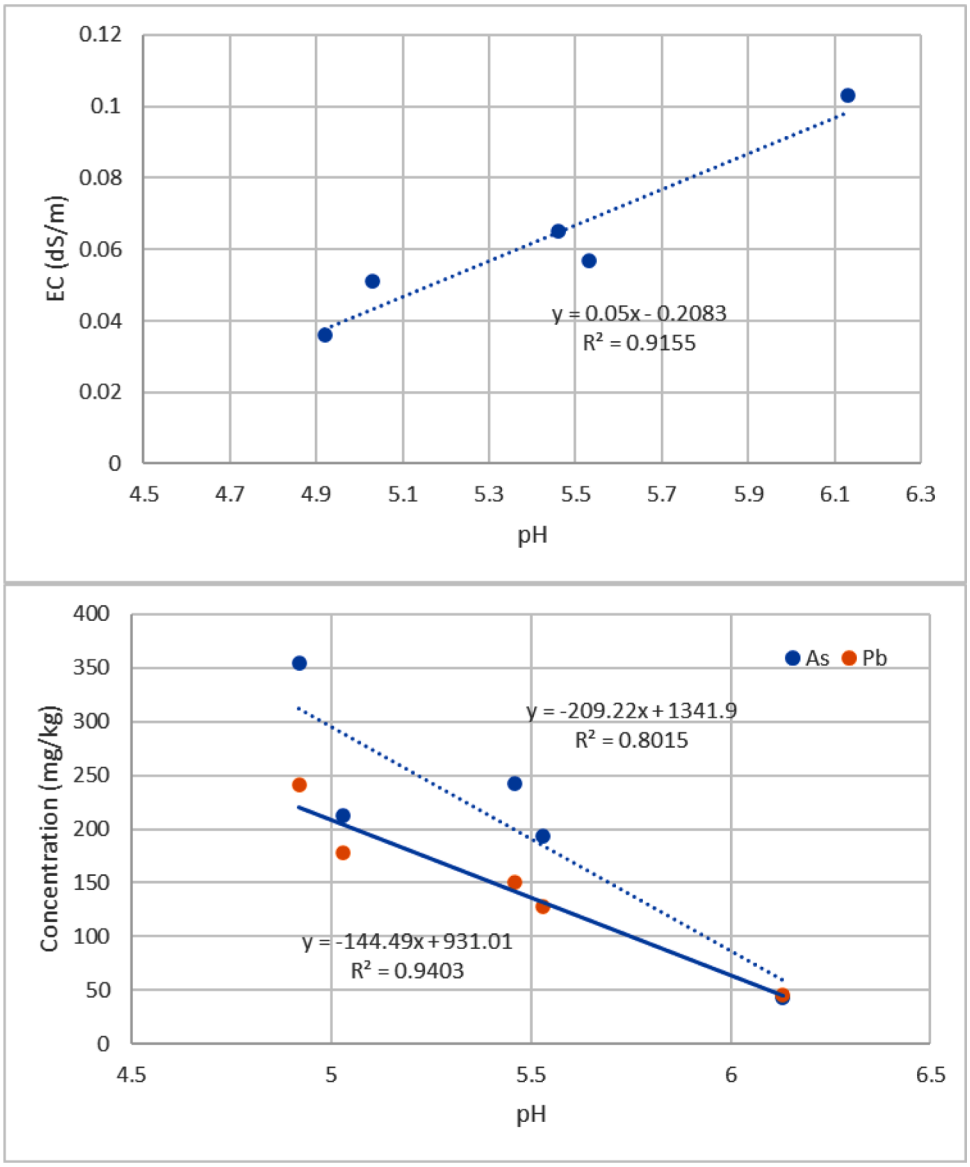

Fig. 2. Relationship between (a) pH and EC and (b) pH and soil-borne As or soil-borne Pb

manufacturing cotton fabrics and brick. The textile dyeing usually requires a bleaching pre-treatment, which involves the use of caustic soda (Asaduzzaman et al., 2016). This affected the pH in the soils, as indicated by that some of the soils in this area had a pH > 8 (Nworie et al., 2019). However, solid wastes from brick making tended to have an acidic pH because it contained residues from combustion of sulfur-bearing coal, which could generate sulfuric acid after oxidation of the reduced sulfur species (Lin, 2012). When these industrial wastes of different sources were mixed in the dumping area, the caustic soda in the textile waste and sulfuric acid in the brick waste went through neutralization reaction.

It was therefore likely that the variation in pH among the five

monitoring locations reflected the variation in the mixing ratio of the acidic brick waste to the alkaline textile waste. Where the mixing ratio was higher, much of H_2SO_4 was not consumed due to insufficient amount of available NaOH, resulting in lower soil pH. The unconsumed H_2SO_4 could then react with soil minerals *e.g.*

$$H_2SO_{4(aq)} + Al(OH)_{3(s)} \rightarrow Al(OH)SO_{4(s)} + 2H_2O \quad (1)$$

This caused partial removal of SO_4^{2-} from the soil solution, which led to the reduction in EC value of the soils. This explains the observed trend that the soil EC decreased with decreasing soil pH (Fig. 2a). The tendency that the soil-borne As and Pb increased with decreasing soil pH (Fig. 2b) is attributable to the increased mixing ratio of acidic brick waste to the alkaline textile waste because these two elements are common heavy metal(loid)s contained in coal (Zhang et al., 2021).

3.2. Seasonal variation in shoot biomass

The plant shoot sample in Subplot 1, Subplot 2, Subplot 3 and Subplot 4 at each monitoring location was collected in August 2018, November 2018, February 2019, and May 2019, respectively. Since the plant growth status within the monitored plot at each monitoring location was deemed as more or less "consistent", the change in the fresh shoot biomass from the 1st to the 4th sampling occasions can be used to demonstrate the seasonal variation in the shoot biomass. It can be seen from Fig. 3 that the average fresh shoot biomass in Subplot 1, Subplot 2, Subplot 3 and Subplot 4 for the five monitoring locations was 535, 438, 361 and 657 g, respectively. This indicates that the grass had its minimum net primary production of shoot at the end of winter and the maximum net primary production of shoot at the end of spring, reflecting the strong control of shoot growth by climatic conditions in the Greater Manchester. Everwand et al. (2014) monitored seasonal variation in grass biomass in the Southeastern England and found that the maximum net primary production of shoot occurred in spring-summer period, which was similar to what was found in this study.

Under shoot-cutting and regrowth conditions, the fresh shoot biomass collected in Subplot 1 at the sampling occasion in August 2018, November 2018, February 2019, and May 2019 was 535, 302, 139 and 473 g, respectively. The net primary production rate of shoot during the autumn was approximately 10 g/m^2/day. And this was reduced to 4.6 g/m^2/day in the winter, which was attributable to the inhibited growth of shoot due to the decrease in temperature. The increase in temperature during the spring markedly enhanced the growth of shoot with a net primary production rate at about 15.7 g/m^2/day. The additional annual shoot biomass yield as a result of seasonal harvest practice was 914 g/m^2.

3.3. Seasonal variation in shoot-borne heavy metal(loid)s

There were different seasonal variation patterns observed for different heavy metal(loid)s (Table 2). No shoot-borne As was detected in the summer but it then increased continuously over time and reached the maximum in the spring. For Cd, the maximum value (4.58 mg/kg) occurred in the summer but markedly dropped to very low levels (below 0.2 mg/kg) in the autumn and winter, and then bounced to above 1.5 mg/kg in the spring. The seasonal variation in Cr was relatively small with the maximum (3.08 mg/kg) occurring in the autumn and the minimum (1.76 mg/kg) occurring in the winter. Cu and Mn had a similar seasonal variation pattern and the shoot-borne metals tended to decrease from the summer to the autumn/winter to the spring. Ni had the minimum in the summer but then maintained at a value ranging from 2.09 to 2.51 mg/kg. The seasonal variation in the shoot-borne Pb was not remarkable with a range of 1.02-1.46 mg/kg. The shoot-borne Zn had the maximum (74.4 mg/kg) in the summer but was reduced to

Table 2
Heavy metal(loid)s in the shoot (mg/kg on a dry weight basis) of the herbaceous plants on the four sampling occasions during the 1-year monitoring period under non-regrowth conditions

Element	Aug-18	Nov-18	Feb-19	May-19	Maximum tolerable level*
As	0.00±0.00	0.83±0.74	1.02±0.65	1.17±0.65	50
Cd	4.58±4.77	0.19±0.10	0.14±0.14	1.68±0.94	0.5
Cr	2.79±1.10	3.08±1.05	1.76±0.74	2.73±1.09	3000
Cu	23.2±14.5	11.8±6.87	15.7±3.31	7.30±1.52	100
Mn	354±129	281±138	191±99.3	116±54.2	1000
Ni	0.50±0.46	2.09±0.62	2.51±0.36	2.30±1.16	50
Pb	1.02±0.59	1.46±0.22	1.30±0.60	1.30±1.26	30
Zn	74.4±13.2	42.8±6.23	44.7±10.9	40.0±10.8	500

* According to Madejón et al. (2006)

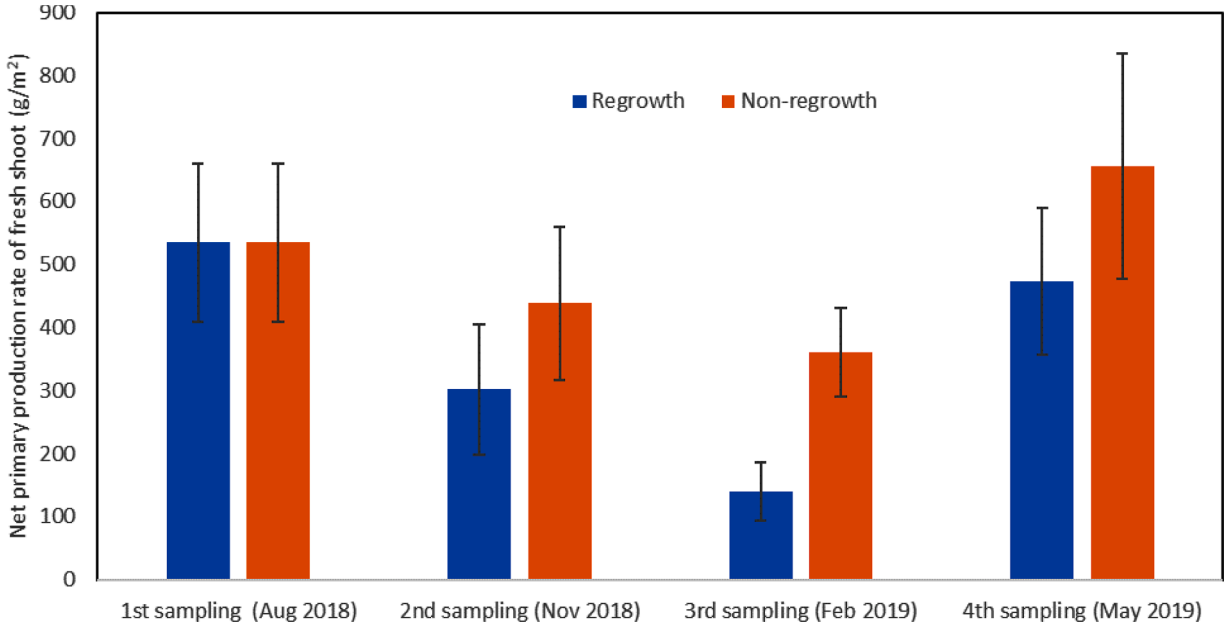

Fig. 3. Seasonal variation in net primary production of fresh shoot biomass under non-regrowth and shoot cutting-regrowth conditions

about 40 mg/kg in the other 3 seasons. Since the average pH in the soils at the monitoring locations was above 5, the solubility of various heavy metal(loid)s in the bulk soils was low. Consequently, solubilization of the soil-borne heavy metal(loid)s by root-released low-molecular-weight organic acids in the rhizosphere was likely to play a key role in regulating the uptake of the heavy metal(loid)s by the plant. It is known that root exudate-borne low-molecular-weight organic acids vary seasonally (Van Hees et al., 2000). Therefore, the seasonal variation in the shoot-borne heavy metal(loid)s was likely to partially reflect the seasonal variation in the low-molecular-weight organic acids in the soils.

Under shoot-cutting and regrowth conditions, the As in the new shoot was 0.82 mg/kg in the autumn, which was an increase from that in the summer. The new shoot in the winter had the maximum As concentration (1.77 mg/kg) and the new shoot-borne As in the spring decreased to 0.76 mg/kg. The seasonal variation pattern in the shoot-borne Cd was consistent with that for the non-regrowth circumstance. Similar to the non-regrowth conditions, the maximum for the shoot-borne Cr occurred in the autumn and the seasonal variation in shoot-borne Cr was relatively small. The shoot-borne Cu showed the same seasonal variation pattern as that under non-regrowth condition. Like the non-regrowth conditions, the shoot-borne Mn tended to decrease from the autumn to the spring except that the maximum value occurred in the autumn. The shoot-borne Ni was very similar between the cutting-regrowth and non-regrowth conditions except in the winter when the shoot-borne Ni was much higher in the latter than in the former. Similar to the non-regrowth condition, the seasonal variation in the shoot-borne Pb was also small with the maximum value occurring in the autumn. In contrast with the non-regrowth condition, the shoot-borne Zn consistently decreased from the summer to the autumn to the winter and to the spring (Table 3). These results suggest that seasonal shoot-regrowth did not markedly affect the accumulation of various heavy metal(loid)s in the shoots.

The concentration of shoot-borne heavy metal(loid)s was below the maximum tolerable level set for cattle (Madejón et al., 2006) except for Cd during spring-summer (Tables 2 and 3). These results suggest that although the soil-borne As and Pb in the study area well exceeded the threshold values, they seemed not to pose a major threat to wild or grazing animals when it comes to the health effects of forage consumption. The excessive amounts of shoot-borne Cd detected during the spring-summer despite that the average concentration of soil-borne Cd was below the threshold value (1 mg/kg) suggest that the use of soil-borne Cd threshold value for assessing its environmental risk is not sufficient. The seasonal variation pattern for removal rate of Cd, Cr, Cu, Pb and Zn (Table 4) was similar to that for the net primary production of fresh shoot biomass (Fig. 3), suggesting the strong control of biomass yield on the phytoextracting effects of these metals. Due to the fact that no As was detected and the smaller amounts of Ni was detected in the shoots collected in August 2018, the removal rate of these two elements was 0 and lower than that in other seasons, respectively, in spite of the observed highest fresh biomass.

Table 3
Heavy metal (loid)s in the shoot (mg/kg on a dry weight basis) of the creeping bentgrass on the four sampling occasions during the 1-year monitoring period under cutting-regrowth conditions

Element	Aug-18	Nov-18	Feb-19	May-19	Maximum tolerable level
As	0.00±0.00	0.82±0.78	1.77±0.81	0.76±0.23	50
Cd	4.58±4.77	0.32±0.10	0.31±0.59	1.25±0.26	0.5
Cr	2.79±1.10	3.20±0.76	2.23±0.61	1.90±0.55	3000
Cu	23.2±14.5	12.4±3.16	19.5±4.38	6.90±2.92	100
Mn	354±129	390±176	197±103	108±43.5	1000
Ni	0.50±0.46	2.11±0.30	4.00±0.59	2.11±1.00	50
Pb	1.02±0.59	1.90±0.45	1.26±1.02	1.06±0.51	30
Zn	74.4±13.2	52.5±16.3	41.1±7.86	32.9±3.29	500

Table 4
Seasonal variation in the removal rate of various soil-borne heavy metal(loid)s by the creeping bentgrass

Element	August 2018	November 2018	February 2019	May 2019
As	0	0.030	0.027	0.054
Cd	0.458	0.012	0.005	0.089
Cr	0.279	0.118	0.033	0.135
Cu	2.320	0.457	0.293	0.490
Mn	35.40	14.39	2.955	7.668
Ni	0.050	0.077	0.060	0.149
Pb	0.102	0.070	0.019	0.075
Zn	7.440	1.937	0.616	2.336

The heavy metal(loid) removal from the soils via seasonal shoot harvest was 0.11, 0.56, 0.57, 3.56, 60.4, 0.34, 0.27 and 12.3 mg/m^2 for As, Cd, Cr, Cu, Mn, Ni, Pb and Zn, respectively. For the topsoil layer (0-15 cm) with an estimated bulk density of 1.5 g/cm^3, the total amount of various heavy metal(loid)s within the 1 m^2 subplot was 47025, 139, 4005, 8415, 37125, 2207, 33525 and 6682 mg/kg, respectively. This means that during the 1-year monitoring period, only 0.0002, 0.4014, 0.0142, 0.0423, 0.1627, 0.0154, 0.0008 and 0.1840% of the total metal (loid)s were removed from the soil by the plant shoots for As, Cd, Cr, Cu, Mn, Ni, Pb and Zn, respectively. These results suggest that except for Cd, Mn and Zn, phytoextraction literally had negligible effects on removing the investigated heavy metal(loid)s from the contaminated soils. The seasonal shoot-borne heavy metal(loid) data can be used as an important indicator for estimation of the fluxes of metals in ecosystem and to ensure that the maximum amount of heavy metal(loid)s is removed with the harvest during phytoextraction process.

3.4. Plant uptake of heavy metal(loid)s

The average bioaccumulation factor for the investigated heavy metal (loid)s was in the following decreasing order: Zn > Mn > Cu > Cr > Ni > Cd > Pb > As (Fig. 4a). The soil-borne heavy metal(loid)s bound to iron and manganese oxides were subject to mobilization upon attack by low-molecular-weight organic acids via reduction and acidification (Qin et al., 2018). Therefore, it is likely that the phytoavailability of heavy metals and As in the rhizospheric soils was enhanced by the low-molecular-weight organic acids secreted from the plant roots. The higher rate of soil-root translocation for Zn and Mn could be attributed to their higher mobility under LMWOA-driven solubilization while the lower soil-root translocation rate for Pb and As was due to the relatively low solubility (Nworie et al., 2017; Onireti et al., 2017; Qin et al., 2018).

It is interesting to note that the translocation factor for Cd was over 10 under either non-regrowth or cutting-regrowth conditions (Fig. 4b and c) although the bioaccumulation factor was smaller than 0.5 (Fig. 4a). The extremely high rate of root-shoot translocation makes the creeping bentgrass growing in the monitoring area an ecotype that can be used for phytoextraction of Cd-contaminated soils although it is not considered as a Cd-hyperaccumulating plant by definition due to the low concentration of the shoot-borne Cd (Reeves et al., 2018). However, it needs to be mentioned that the average concentration of soil-borne Cd was below 1 mg/kg, which could be a limiting factor for uptake of substantial amounts of Cd in the rhizosphere by the plant roots. It is likely that much higher concentration of shoot-borne Cd could be achieved if this creeping bentgrass ecotype is grown in heavily Cd-contaminated soils. It is therefore worthwhile to perform further experiments to examine the effect of Cd dose on the accumulation of Cd in the shoot tissue for this bentgrass ecotype.

The findings obtained from this study have implications for risk management of the industrial waste-turned contaminated soils. The seasonal shoot-borne heavy metal(loid) data can be used as an important indicator for estimation of the fluxes of metals in ecosystem. The use of soil-borne Cd threshold value for assessing its environmental risk is not

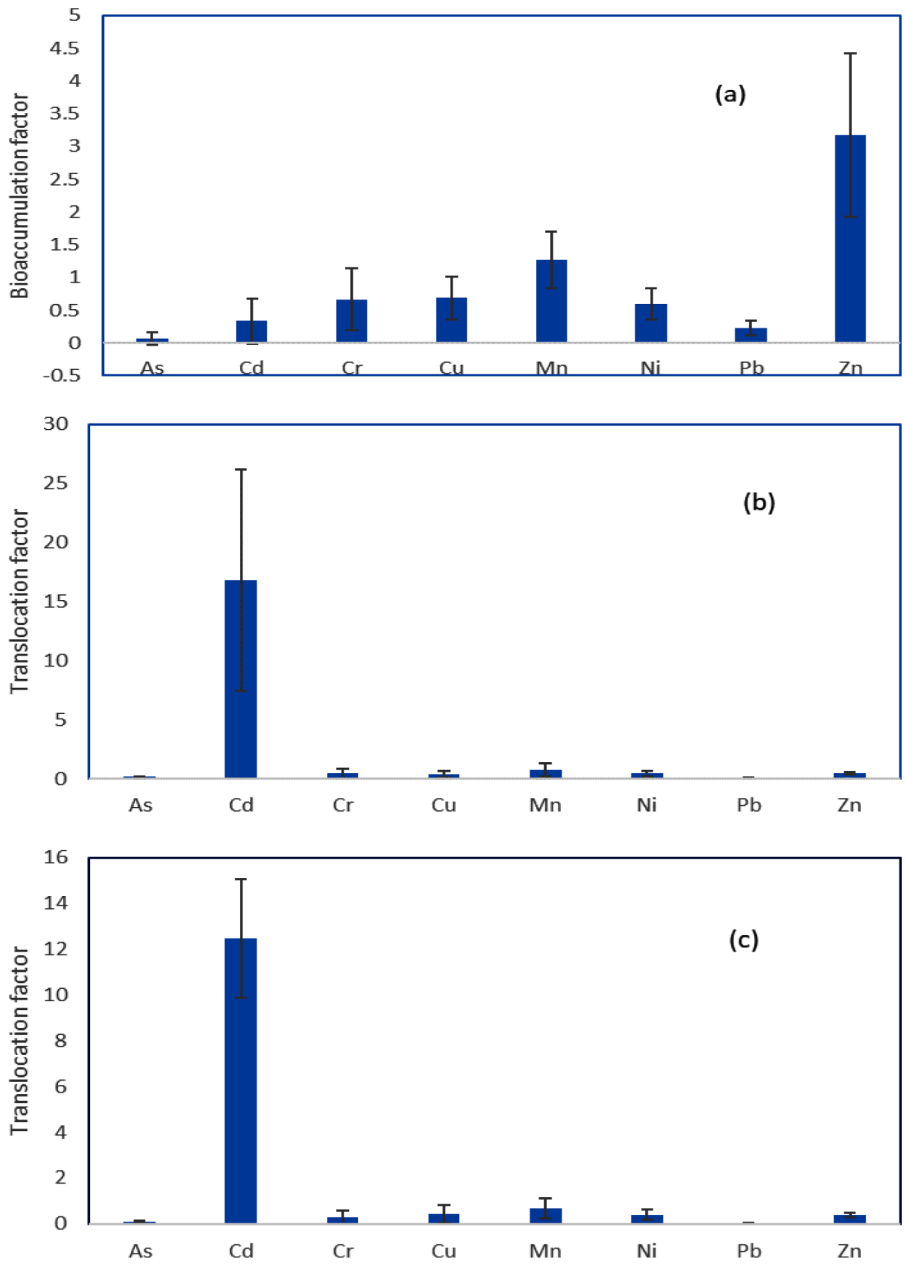

Fig. 4. Comparison of (a) bioaccumulation factor, (b) translocation factor under non-regrowth condition, and (c) translocation factor under cutting-regrowth condition for the creeping bentgrass grown in the soils at the monitoring locations

sufficient. Further work is therefore needed to close the relevant research gaps in order to improve the environmental risk assessment system.

4. Conclusion

The shoot growth of the monitored creeping bentgrass was controlled by climatic conditions, having its minimum net primary production of shoot at the end of winter and the maximum net primary production of shoot at the end of spring. Different heavy metal(loid)s in the shoot tissue showed different seasonal variation patterns. Seasonal shoot cutting-regrowth did not markedly affect the accumulation of various heavy metal(loid)s in the shoots. The concentration of shoot-borne heavy metal(loid)s was below the maximum tolerable level set for cattle except for Cd during spring-summer. The soil-borne As and Pb seemed not to pose a major threat to wild or grazing animals despite that they well exceeded the threshold values for forage consumption. In contrast, the excessive amounts of Cd present in the shoot tissues during spring-summer although the soil-borne Cd was below the threshold value. The seasonal variation pattern for removal rate of Cd, Cr, Cu, Pb and Zn was strongly controlled by seasonal variation in biomass yield. Phytoextraction literally had negligible effects on removing the investigated heavy metal(loid)s from the contaminated soils except for Cd, Mn and Zn. The average bioaccumulation factor for the investigated heavy metal(loid)s was in the following decreasing order: Zn > Mn > Cu > Cr > Ni > Cd > Pb > As . The translocation factor for Cd was over 10 under either non-regrowth or cutting-regrowth conditions although the bioaccumulation factor was smaller than 0.5.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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